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# Codeposition of Wear-Resistant Particles with Chromium

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Rock Island Weapons Laboratory  
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Prepared for  
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**U. S. DEPARTMENT OF COMMERCE, Frederick B. Dent, Secretary**  
**NATIONAL BUREAU OF STANDARDS, Richard W. Roberts, Director**



## TABLE OF CONTENTS

*Abstract*

*Objective*

|                                                                  | Page  |
|------------------------------------------------------------------|-------|
| INTRODUCTION. . . . .                                            | 1     |
| PROCEDURE . . . . .                                              | 2     |
| TESTS AND RESULTS . . . . .                                      | 2     |
| Various Hard Particles . . . . .                                 | 2     |
| Bath Life Test . . . . .                                         | 4     |
| Various Additives. . . . .                                       | 6     |
| Corrosion Protective Deposits Containing Hard Particles. . . . . | 7     |
| Cadmium . . . . .                                                | 7     |
| Zinc. . . . .                                                    | 8     |
| Gun Tube . . . . .                                               | 9     |
| Heat-Treated Deposits. . . . .                                   | 10    |
| DISCUSSION. . . . .                                              | 12    |
| CONCLUSIONS . . . . .                                            | 15    |
| BIBLIOGRAPHY. . . . .                                            | 16    |
| FIGURES . . . . .                                                | 17-34 |



### Abstract

Several new hard particles were tried with the object of improving wear-resistance of chromium deposits containing included particles over the best previously tried material, tetra-boron carbide. Only hexa-boron carbide was slightly better. During a bath-life test 5100 ampere-hours per liter were run through a particle-including chromium bath. Build-up of products of the monovalent-cation additive used was detected but bath performance could be restored to normal by their removal. Heat treatment of deposits showed reduction in wear-resistance of deposits heated to 400°C or over. A caliber 0.30 tube was plated with chromium having included particles with relatively good particle distribution throughout the bore. Deposits of cadmium and zinc with included hard particles showed some improvement in wear-resistance.



### Objective

The experiments described in this report are attempts to improve the wear-resistance of deposited coatings, mainly chromium, by incorporating hard particles in the deposits with the addition of inorganic additives in the form of monovalent cations to the plating baths which contain the hard particles in suspension.



## CODEPOSITION OF WEAR-RESISTANT PARTICLES WITH CHROMIUM

### INTRODUCTION

Previous annual reports on this project are dated January 26, 1971, and March 1, 1972. The tests (170) described in this report are a continuation of the experiments for codepositing inorganic hard particles with chromium. The main objective of the experiments made during this period was the development of a practical bath and procedure for the incorporation of hard particles in chromium on a more or less production basis. Further tests were made using inexpensive chemicals as bath additives and several more types of hard particles were tested. A bath-life test was run to determine the effect of additives and particles on the longevity of the chromium plating bath. As a practical experiment, a gun tube was plated with chromium incorporating hard particles. In addition to chromium, deposits of cadmium and zinc were made which included hard particles in cyanide baths. Test deposits were made on vertical cathodes of copper or steel and a few were heat-treated after deposition to check the effects of heating on wear, adhesion, and structure of the deposit. All the hard particles tried were incorporated in chromium deposits at least to some degree when any of the monovalent cations tried were present in the bath. Particles were included in the cadmium and zinc deposits without additives although addition of thallium salts to the zinc bath increased the amount of particles included. Ammonium nitrate was effective as an additive in the chromium bath and only after several thousand ampere-hours per liter of bath did deterioration of the bath begin as evidenced by the decreased wear-resistance of the deposits.



## PROCEDURE

The experimental equipment and the procedure for running the tests were the same as for the previous work. To summarize, a 3-3/4" diameter copper or steel disc, about 30 mils thick, was plated using a similar sized lead anode parallel to the disc cathode with about 3/4" separation. A one-liter chromium bath was used to which particles and chemicals were added as the particular test required. Duration of deposition was varied according to the current density used to give a deposit about 5 mils thick. The deposit was tested for wear-resistance on a Tabor Abraser using the CS-17 rubber bonded silicon carbide abrasive wheels. The deposit was cross-sectioned and mounted in plastic for polishing, microscopic examination, photographing and making hardness measurements. The average amount of inclusions in a deposit was determined by dissolving the chromium from one-half of the disc, filtering out the residue, drying, and weighing.

## TESTS AND RESULTS

### Various Hard Particles

Up to this point in our investigation, chromium deposits with incorporated diamond particles resulted in the best wear-resistance. The next best wear characteristics were given by incorporated tetra-boron carbide particles. An effort was made to find particles that would impart greater wear-resistance to chromium deposits than  $B_4C$ . One of the large abrasive suppliers especially prepared without charge six super-hard particles and a seventh type of hard particle was purchased from another company. The particles were as follows:  $AlB_{12}$ ,  $B_4C$ ,  $B_6C$ ,  $CrB_2$ ,  $\beta Si_3W_4$ ,  $TiB_2$ , and  $TiC$ . The average size of the particles was about 25  $\mu m$ . Scanning electron



micrographs of two of the types of particles (Fig. 1) show a rather wide range of sizes which is not considered detrimental for our purpose.

The particle resulting in the best wear of a chromium deposit by a small margin was  $B_6C$ . The special  $B_4C$  and the  $AlB_{12}$  were very close in imparting wear-resistance. Commercial silicon carbide particles of about 15  $\mu m$  in size were used for comparison. The 200 g/l  $CrO_3$  bath and a vertical cathode were used for all tests. Three or four runs were made using each type of particle at one or two temperature-current densities and with two types of chemical additives. A summary giving the averages of the results for tests of each type of particle is given below:

| <u>Particle</u> |          | <u>Deposit</u>         |           |            |
|-----------------|----------|------------------------|-----------|------------|
| Type            | Hardness | Hardness               | Wear Loss | Inclusions |
| $AlB_{12}$      | 2300 KHN | 675 KHN <sub>200</sub> | 7.7 mg    | 0.18 wt    |
| $B_4C$          | 2800     | 669                    | 7.5       | 0.27       |
| $B_6C$          | 3000     | 695                    | 6.3       | 0.30       |
| $\beta Si_3N_4$ | 3000     | 677                    | 12.9      | 0.33       |
| $CrB_2$         | 3500     | 604                    | 11.2      | 0.61       |
| $TiB_2$         | 2700     | 662                    | 7.8       | 0.59       |
| $TiC$           | 2500     | 640                    | 12.2      | 0.83       |
| $SiC$           | 2500     | 749                    | 10.2      | 0.85       |
| Glass powder    | ----     | 616                    | 11.3      | 0.20       |

The detailed data from the tests indicated that specific combinations of plating conditions and additives resulted in increased inclusion rates of some particles. For example,  $TiB_2$  was included in substantially greater amounts using  $LiNO_3$  at 45°/30 asd than at 55/50. Using  $TlNO_3$  and  $LiNO_3$ , larger amounts of  $TiC$  were included at 45/30 than at 55/50. These instances conform with the general observation throughout the program that fewer particles are normally included at higher current density and temperature conditions but this is not true for all combinations of particles and additives. Therefore, it cannot be taken for granted that an additive or a



set of plating conditions will result in the best particle inclusion rate for a given particle because it is best for several others.

None of these special hard particles showed enough improvement in wear-resistance when included in chromium to warrant their use in place of some of the best of the more readily available particles already tested although the  $B_6C$  shows some superiority over all the others tested except diamond.

During the tests of the  $CrB_2$  particles, some of the thallium and cesium additions to the chromium baths were made in the crystal form. The usual procedure was to add these components as a water solution in four equal increments during the run. Additions as crystals did not form the usual yellow precipitate and the effectiveness of the additives seemed to extend throughout the run of 4 or 5 hours without partial periodic addition to the bath as had been previously practiced. In a water solution of  $CrO_3$  the crystals were observed to dissolve very slowly.

#### Bath Life Test

The initial phase of this test consisted of eight runs. A new bath was used for each of the first three runs; then five consecutive runs were made in the same bath. All eight tests were made with 30 g/l  $B_4C$  and 3 g/l  $TlNO_3$  in the baths. The wear-resistance was good for the three runs in the new bath, about one-half the weight loss for hard, bright chromium without inclusion, and the results are quite close. The tests in the "used" bath indicate a slight decrease in wear-resistance for each successive run as an increasing amount of current is put through the solution as shown in Fig. 2. Bath component concentration levels were maintained and no substantial decrease in the amount of included material in



in the deposits occurred throughout the test. Since the trivalent chromium content of the bath remained within acceptable levels, it is probable that the slight decrease in wear-resistance of successive deposits was due to build-up in the bath of Tl or Tl compounds. Deposits and amounts of included material did not appear to be adversely affected.

The second phase of the bath-life test consisted of 58 tests for a total of 5100 ampere-hours per liter of chromium plating solution. Components of the solution were renewed as necessary to maintain the nominal bath composition of 200 g/l  $\text{CrO}_3$ ,  $2\text{H}_2\text{SO}_4$  and 30 g/l  $\text{B}_4\text{C}$ . Ammonium nitrate at 1 g/l was used as the monovalent cation additive for most of these tests. Near the end of the experiment several tests were made with addition of  $\text{NH}_4\text{NO}_3$  and hardness of the chromium deposit returned to about 1000 KHN<sub>200</sub> and inclusions in the chromium dropped below 0.1 wt% indicating approximately normal deposits that would be expected from a standard chromium bath. However, after about 3200 amp-hours per liter had been passed through the bath, the spread of wear-resistance values obtained increased substantially (as shown in Fig. 3) and the average wear-loss had about doubled at the end of the test or at 5100 ampere-hours. There were visible encrustations on areas of the bath container where the bath was subject to evaporation. This was assumed to be the result of the build-up of  $\text{NH}_4\text{NO}_3$  or its decomposition products. It was definitely not  $\text{CrO}_3$ . At the end of this series of tests, a total of nearly 40 grams of  $\text{NH}_4\text{NO}_3$  had been added to the bath.

The above indicates that there is probably a limit to the life of a chromium bath when using  $\text{NH}_4\text{NO}_3$  as an additive beyond which deposit properties would not be acceptable. For all practical purposes even 3200 ampere-



hours per liter of bath represents a very long bath life in the practical chromium plating bath. In addition it is entirely possible that the products of the additive could be removed from the bath by a simple procedure such as cooling and decanting as they seem to be much less soluble than  $\text{CrO}_3$ .

During the bath-life experiment the use of a new wear-test abraser was started. Comparison of the results obtained on the new and old machine showed some difference in wear-resistance values so a factor was used to make results compatible.

#### Various Additives

A number of runs were made using the additives previously tested to some extent. As indicated in the section above,  $\text{NH}_4\text{NO}_3$  was used in a considerable number of tests and was found to be effective for incorporating particles in chromium deposits. However, the bath would tolerate only about one-third as much  $\text{NH}_4\text{NO}_3$  as  $\text{TlNO}_3$  and still produce continuous, hard deposits. More runs were also made using  $\text{LiNO}_3$  and  $\text{CeNO}_3$  and, of course,  $\text{TlNO}_3$ . A general summary of the relative performance of the additives during these tests is shown in Fig. 4 and is tabulated below:

| Additive                 | No. of Runs<br>in Av. | Most<br>Inclusions<br>(wt %) | Av. Inclusions<br>(wt %) | Least<br>Wear-Loss<br>(mg) | Av.<br>Wear-Loss<br>(mg) |
|--------------------------|-----------------------|------------------------------|--------------------------|----------------------------|--------------------------|
| $\text{NH}_4\text{NO}_3$ | 39                    | 3.89                         | 0.762                    | 3.9                        | 8.2                      |
| $\text{LiNO}_3$          | 12                    | 2.29                         | 0.60                     | 6.4                        | 11.3                     |
| $\text{CeNO}_3$          | 4                     | 1.65                         | 1.26                     | 8.2                        | 10.0                     |
| $\text{TlNO}_3$          | 45                    | 1.41                         | 0.41                     | 3.0                        | 8.6                      |



All of the above deposits were made on vertical surfaces but include several different types of particles and plating conditions of from 45°C/20 asd to 55/50. Several, but not necessarily all, of the conditions were used for each type of additive. Figs. 4, 5, and 6 show the relative amounts of inclusions and wear-loss respectively for lithium nitrate as compared to thallium nitrate for runs under similar conditions. The lithium shows wider fluctuations in both categories than does thallium nitrate.

#### Corrosion Protective Deposits Containing Hard Particles

Cadmium. A number of cadmium and zinc deposits were made which incorporated  $B_4C$  and  $Al_2O_3$  hard particles in an attempt to improve the wear-resistance of a soft, protective coating. No chemical additives were needed to include particles in cadmium and zinc deposits although one-half to one gram per liter of thallium salts in the bath increased the amount of included material in zinc.

The cadmium specimens were plated in a bath of the following nominal composition:

|                               |          |
|-------------------------------|----------|
| Cadmium oxide, CdO            | 22.5 g/l |
| Sodium cyanide, NaCN          | 100      |
| Sodium hydroxide, NaOH        | 14       |
| Gulac (organic grain refiner) | 0.4      |

To this bath was added the  $Al_2O_3$  and  $B_4C$  in varying amounts from 10 to 30 g/l. The current density used for a particular deposit seemed to have more effect on wear-resistance than the type or amount of hard particle incorporated. All runs were plated at about 24°C. Below is a summary of the cadmium deposits tested:



| Current Density<br>(asd) | No. Runs | Type of Particles              | Max. Inclusions<br>(wt %) | Av. Inclusions<br>(wt %) | Least Wear-Loss<br>(mg) | Av. Wear-Loss<br>(mg) |
|--------------------------|----------|--------------------------------|---------------------------|--------------------------|-------------------------|-----------------------|
| 1                        | 2        | --                             | --                        | --                       | 53.8                    | 55.9                  |
| 1                        | 2        | B <sub>4</sub> C               | 0.69                      | 0.67                     | 29.4                    | 39.1                  |
| 2                        | 4        | "                              | 1.06                      | 0.98                     | 19.3                    | 23.9                  |
| 3                        | 1        | "                              | --                        | 1.11                     | --                      | 27.8                  |
| 4                        | 1        | "                              | --                        | 1.48                     | --                      | 32.0                  |
| 5                        | 1        | "                              | --                        | 1.08                     | --                      | 25.2                  |
| 1                        | 2        | Al <sub>2</sub> O <sub>3</sub> | 0.58                      | 0.38                     | 53.8                    | 64.7                  |
| 2                        | 4        | "                              | 0.64                      | 0.58                     | 33.3                    | 43.8                  |
| 3                        | 3        | "                              | 0.88                      | 0.62                     | 34.8                    | 36.3                  |
| 5                        | 1        | "                              | --                        | 0.60                     | --                      | 47.1                  |

The improvement in wear-loss for deposits with included particles was better than two to one over deposits without particles for the best series of tests. The B<sub>4</sub>C particles were incorporated more readily and resulted in the greatest improvement in wear-resistance. Average inclusions per run for B<sub>4</sub>C was 1.06 wt %, for Al<sub>2</sub>O<sub>3</sub>, 0.55 wt %. Average wear-loss for B<sub>4</sub>C was 29.6 mg, for Al<sub>2</sub>O<sub>3</sub>, 48.0 mg. Figures 7-9 are graphic presentations of data from tests of Cd deposits. Refinement of bath composition and plating conditions could quite possibly further improve the wear-resistance of cadmium coatings.

Zinc. The zinc bath used had the following composition:

|                                                                   |         |
|-------------------------------------------------------------------|---------|
| Zinc sulfate, ZnSO <sub>4</sub>                                   | 240 g/l |
| Ammonium chloride, NH <sub>4</sub> Cl                             | 15      |
| Ammonium sulfate, (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> | 30      |
| Licorice (grain refiner)                                          | 1       |

To this bath up to 30 g/l B<sub>4</sub>C and Al<sub>2</sub>O<sub>3</sub> particles were added. Also, several tests were run in a zinc bath containing thallium salts as well as hard particles which did increase the amount of inclusions in the deposits. A series of runs was made in the zinc bath with varying amounts of particles in the bath and at several current densities as well as a



few runs using thallium. A summary of the tests is shown below:

| Current Density (asd) | No. Runs | Type of Particles              | Max. Inclusions (wt %) | Av. Inclusions (wt %) | Least Wear-Loss (mg) | Av. Wear-Loss (mg) |
|-----------------------|----------|--------------------------------|------------------------|-----------------------|----------------------|--------------------|
| 2                     | 2        | --                             | --                     | --                    | 34.9                 | 36.5               |
| 3                     | 2        | --                             | --                     | --                    | 40.6                 | 42.0               |
| 2                     | 1        | Al <sub>2</sub> O <sub>3</sub> | --                     | 0.13                  | --                   | 28.4               |
| 3                     | 4        | "                              | 1.05                   | 0.50                  | 30.3                 | 42.9               |
| 5                     | 1        | "                              | --                     | 0.13                  | --                   | 22.5               |
| 2                     | 3        | B <sub>4</sub> C               | 1.96                   | 0.99                  | 20.5                 | 25.9               |
| 3                     | 5        | "                              | 0.43                   | 0.31                  | 19.5                 | 23.2               |
| 5                     | 2        | "                              | 0.59                   | 0.43                  | 26.0                 | 26.7               |
| 2                     | 4        | B <sub>4</sub> C+Tl.           | 1.82                   | 0.78                  | 21.0                 | 27.7               |
| 3                     | 6        | "                              | 1.79                   | 0.98                  | 17.4                 | 23.3               |
| 5                     | 2        | "                              | 0.58                   | 0.53                  | 23.0                 | 25.2               |

Since the current density seemed to have more effect on the wear-loss than the amount of particles in the bath, all runs at a particular c.d. were averaged together from baths containing ten to thirty g/l of particles. The improvement in wear-resistance for deposits containing hard particles was not as great as for cadmium but there was some improvement at 2 and 5 asd with Al<sub>2</sub>O<sub>3</sub> and with B<sub>4</sub>C in the bath. (See Figures 11 to 13 for graphic representations of the data.)

Thallium increased the amount of included material at 3 asd but was not effective in these tests at 2 and 5 asd. Wear-resistance was very close with or without thallium, about two-thirds that of deposits without inclusions. Average inclusions per run with Al<sub>2</sub>O<sub>3</sub> was 0.32 wt %, with B<sub>4</sub>C, 0.70 wt %. Average wear-loss for Al<sub>2</sub>O<sub>3</sub> was 36.6 mg, for B<sub>4</sub>C, 25.0 mg. Data from deposits formed with thallium in the zinc bath are shown graphically in Figures 14 and 15.

#### Gun Tube

A 0.30 caliber machine gun tube furnished by the Rock Island Weapons Laboratory was plated on the inside with chromium incorporating hard



particles by adding thallium and  $B_4C$  powder to a standard 200 g/l  $CrO_3$  bath. First, several steel tubes of approximately the same inside diameter as the gun tube were plated experimentally to determine the correct equipment or fittings and plating conditions necessary to obtain a more or less uniform coating on the tube bore. To obtain approximately the same deposit thickness distributions as the original chromium plate in the tube bore, 0.0033" at the muzzle and 0.0025" at the breach, it was necessary to form a one-eighth-inch diameter anode from pure silver wire and then copper and lead plate it for protection from attack. Using this anode and a temperature-current density ratio of 45/30, it was found that a reasonably uniform deposit incorporating  $B_4C$  particles could be applied to the simulated gun tubes. The gun tube bore, plated in a vertical position at these conditions, had a deposit thickness at the muzzle of 0.0031" and at the breach, 0.0027". The simulated gun tubes were sectioned and revealed inclusions of hard particles in the rather rough deposit even at the top of the tube. Fig. 16 shows cross-sections at the top and the bottom of one of these test specimens in which the distribution of the chromium was rather poor but otherwise similar to the deposit in the gun tube. It was later learned that the chromium deposit with incorporated particles in the gun tube was broken from the bore surface rather quickly under firing test conditions without much of a determination of its "wearability."

#### Heat-Treated Deposits

Several particle-containing chromium deposits plated on copper were heated in air to determine the effect, if any, on adhesion to the substrate



and wear qualities. After heating, mild bending of the specimens cracked the chromium but no flaking, indicating loss of adhesion, occurred. Wear-resistance was somewhat diminished on those deposits heated above 250°C as is shown in the data below:

| Initial<br>Wear-Loss | Heat-<br>Treatment | Resultant<br>Wear-Loss<br>(mg) |
|----------------------|--------------------|--------------------------------|
| 12.8                 | 400°C - 1 hr       | 17.3                           |
| 13.8                 | " " "              | 17.3                           |
| 10.6                 | 600°C " "          | 15.5                           |
| 13.6                 | 250°C 2 "          | 12.9                           |

The normal heat-treatment of chromium plated parts to relieve possible hydrogen embrittlement of the substrate is in the 200-300°C range so chromium deposits with included particles should not be adversely affected. Cross-sections of the heated deposits are shown in Fig. 17.

#### DISCUSSION

It was rather disappointing to learn that of the several new types of particles tried, only one showed any improvement in wear-resistance over the previously tested  $B_4C$ . The particle giving improved wear when incorporated in chromium was the closely related  $B_6C$  and the improvement was only slight. This means that for top wear-resistance diamond powder must be incorporated in the deposits. The expense of using diamond could be reduced by using a smaller amount in the bath without seriously affecting incorporation rates. It is estimated that as little as 10 or even 5 g/l instead of 30 g/l would be effective in the bath. Since the amount usually included in the deposit is 1 wt % or less, the depletion rate would be minimal. However, in general  $B_4C$  and even  $SiC$  give improved wear-resistance when included in deposits and would probably be effective for most uses.



Particles are included most effectively at 45°C or below and at current densities of 50 and down to 20 asd with the most effective combination for most selections of additives and particles at 45°C and 30 asd. These conditions result in a deposition rate of about 1 mil per hour and reasonable distribution. If required, higher temperatures and current densities include some particles up to about 65°C and 60 asd.

Some types of particles seem to be more readily incorporated than others. This may be related to their ability to become electrically charged. Shape, size, mass, and adsorption may also have some effect. For example, nickel coated diamond is more readily incorporated than uncoated diamond and SiC and  $\text{CrB}_2$  were incorporated more easily and in larger quantities over a range of conditions than some other types that may not be as conductive.

Normally the life of a chromium bath is indefinite, requiring only periodic additions of  $\text{CrO}_3$  to replace deposit and drag-out losses. The life test run on the chromium bath containing additives for the including of particles up to 5100 ampere-hours per liter showed that the only problem was a build-up of the additive or by-products of the additive in the bath. When the bath was treated for removal or reduction in concentration of these by-products, it behaved normally again. The only exception was a bath used with lithium nitrate as an additive. It seemed to contribute to the build-up of  $\text{Cr}_2\text{O}_3$  in the bath and prevent its reduction to  $\text{CrO}_3$  again. Deposits from a bath thus affected were dull and rough and uniformity of coverage was poor.

It is considered that in a large plating bath the use of the other additives would not cause any problems as 5100 ampere-hours per liter of



bath represents a considerable amount of plating in a particle plating operation.

Further tests of several of the additives used, mainly  $\text{NH}_4\text{NO}_3$  and  $\text{CeNO}_3$ , confirmed previous results indicating that  $\text{CeNO}_3$  was most effective for incorporating particles in a chromium deposit with minimal disruption of the structure and characteristics of the chromium. However, it is quite expensive and more common materials such as  $\text{NH}_4\text{NO}_3$  are inexpensive and adequate for practical operations. Probably the ultimate combination according to present results would be  $\text{CeNO}_3$  and nickel coated diamond particles added to a 200 g/l  $\text{CrO}_3$ ,  $2\text{H}_2\text{SO}_4$  bath operated at  $45^\circ\text{C}$  and 30 asd for the best wear-resistant deposit.

Particles were incorporated on vertical cathodes in cadmium and zinc deposits from the cyanide baths used without the use of an additive. However, the use of thallium in the zinc bath enhanced the amount of particles included. It was not tried in the cadmium bath. Wear-resistance was more than doubled for cadmium deposits containing hard particles. Wear-resistance for zinc deposits containing hard particles was improved but only by about 30 to 50%. It is possible that variation of mechanical arrangement of the electrodes and bath composition could considerably increase the amount of included material and thus perhaps the wear-resistance.

Heating the chromium deposits in air oxidized the exposed copper basis material extensively but only treatments at  $400^\circ\text{C}$  and above oxidized the chromium. The reduction in wear-resistance at the higher temperatures was expected as any softening of the chromium matrix reduces wear qualities despite the presence of hard particles which were most likely unaffected by the comparatively low temperatures used.



At the end of the program a few tests were made in a 200 g/l  $\text{CrO}_3$  chromium bath using sodium fluosilicate as a catalyst plus an additive and hard particles. Efficiency was very low and only a coarse, greenish colored deposit was obtained which had completely unsatisfactory wear qualities. There was no time to experiment with other fluoride catalysts or plating bath combinations.

This program for incorporating hard particles in chromium deposits has shown that many monovalent cations are effective when added to the bath in amounts of about 3 g/l or less over a range of plating conditions and even on vertical cathodes. Without these additions no particles are included from the standard chromium bath. However, the additives or the included particles or both result in the deposition of softer, dull deposits under plating conditions that would normally yield hard bright deposits. Wear-resistance is improved over bright, hard deposits only because of the presence of hard particles in the chromium matrix. If additives and conditions could be found that deposited bright, hard chromium with included hard particles, it is fairly certain that the improvement in wear-resistance would be many times that achieved in this program.



### Conclusions

It is apparent from the work done on this program that it is entirely feasible to include hard particles in chromium deposits with a resultant increase in wear-resistance. Properties of the chromium such as hardness and brightness are diminished when particles are included either because of the presence of particles in the deposit or because of the monovalent cation added to the plating bath to effect their inclusion or both.

Inclusions of even less than 1 wt % of hard particles in the chromium deposit can be effective in reducing wear. Boron carbide particles yielded the best wear characteristic, with the exception of diamond, of any particles commercially available with very inexpensive silicon carbide a close second. Bath-life using the additive is reasonably good and no impediment is seen to scaling up the process for practical applications on at least a semi-production basis. Particles are included in deposits on vertical and horizontal surfaces as well as on the inside of tubes using suitable internal anodes using plating conditions within the normal range for chromium deposition.



Bibliography

- M. Viswanathan, Occlusion Plating to Form Nickel Cermets, Metal Finishing 71, 1 (1973).
- H. Brown and T. Tomaszewski, Occlusion Plating of Fluocarbon Resins, U.S. Pat. 3,677,907.
- D. W. Smith and P. D. Groves, A Study of the Mechanisms of Cement Electrodeposition, Trans. Inst. Met. Fin. 50, (1972).





Figure 1. SEM photos of  $B_4C$  (top) and  $B_6C$  hard particles at about 1600X.



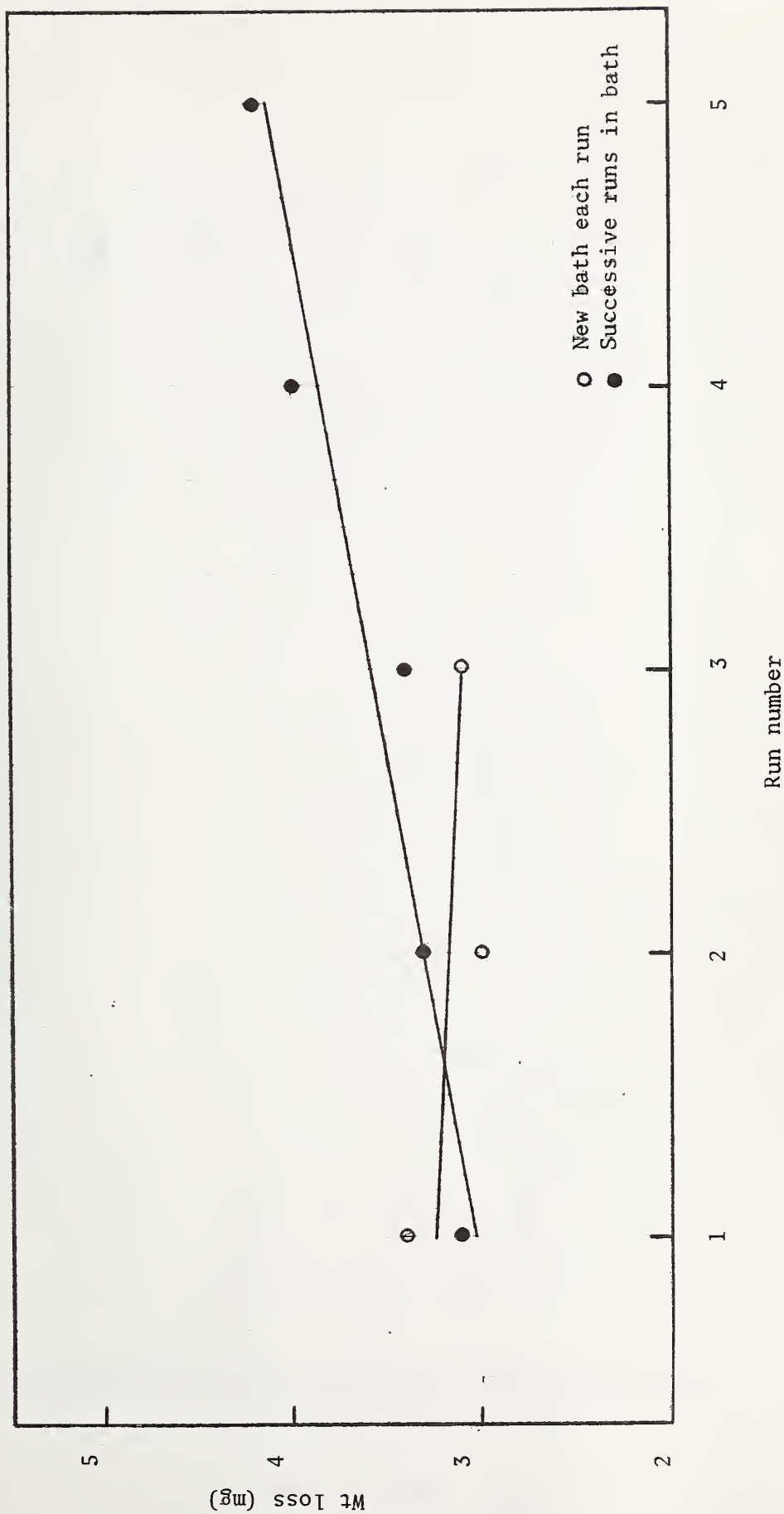


Figure 2. Bath aging effect on wear of deposits plated in a bath containing 3 g/l  $\text{TiNO}_3$  and 30 g/l  $\text{B}_4\text{C}$  at  $45^\circ/30$  asd.



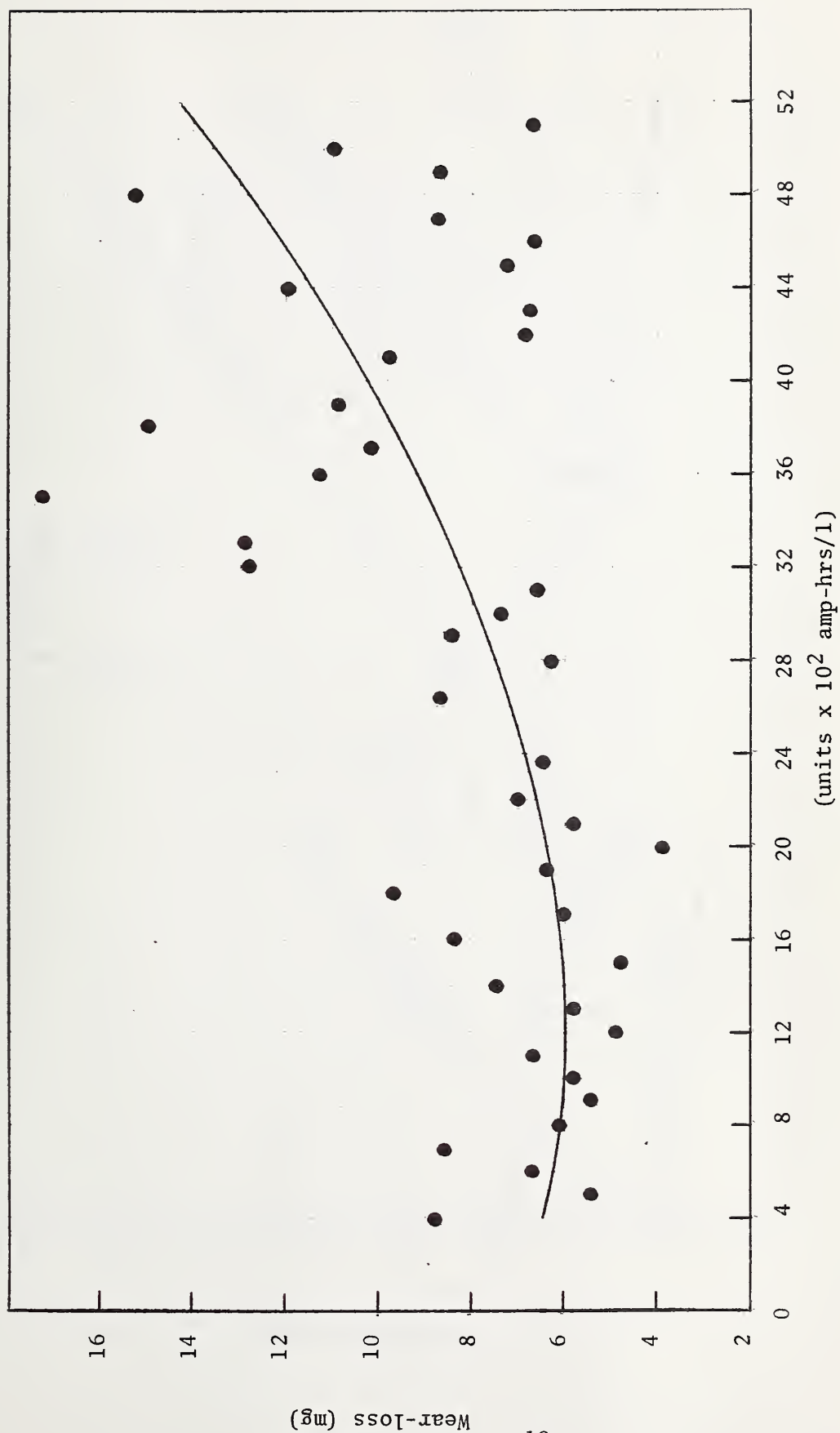


Figure 3. Bath-life test using mainly  $\text{NH}_4\text{NO}_3$  as an additive at plating conditions of 45°C/20 asd to 55/50.



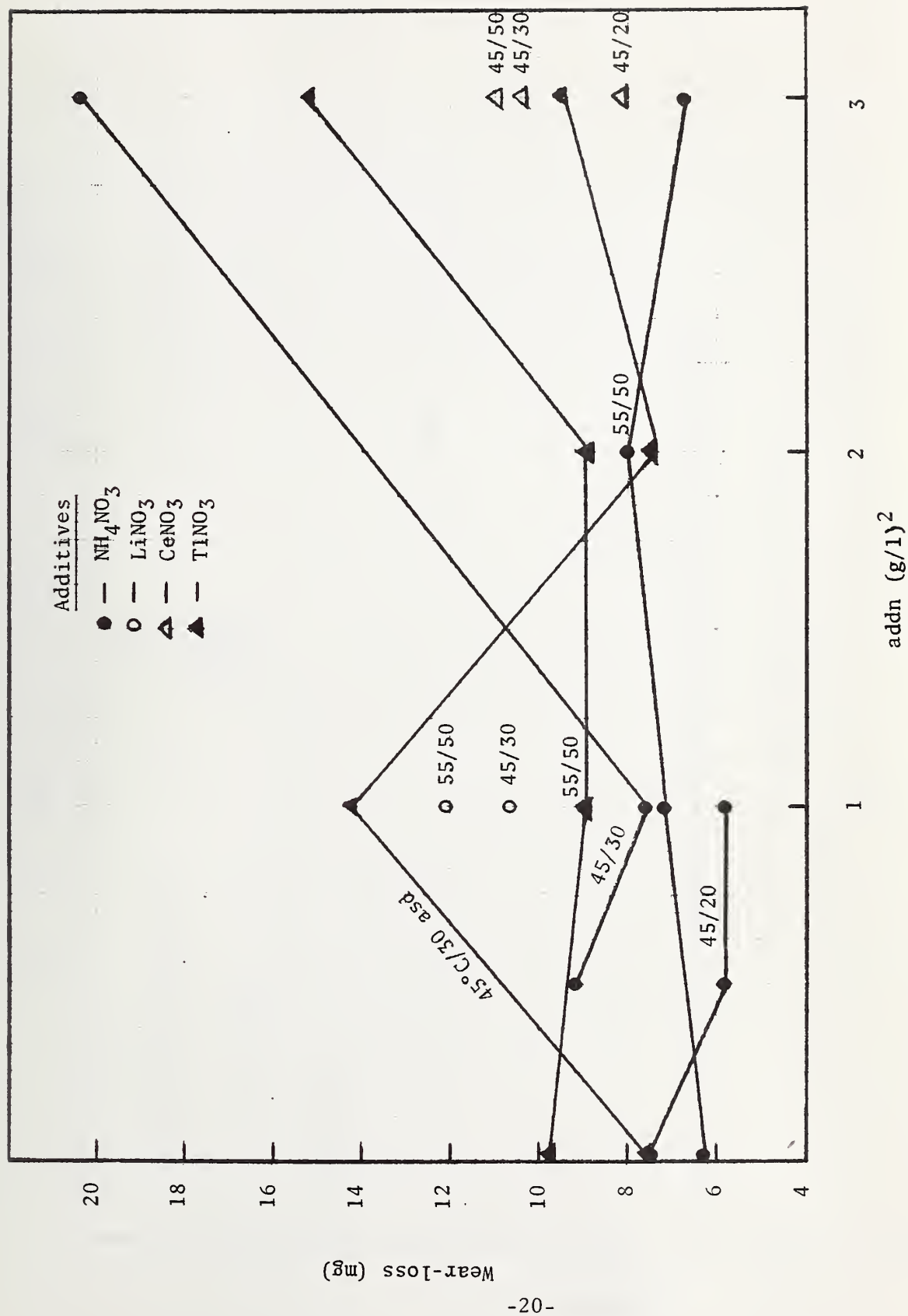


Figure 4. Performance of various additives used in 200 g/l  $\text{CrO}_3$  bath with suspended particles.



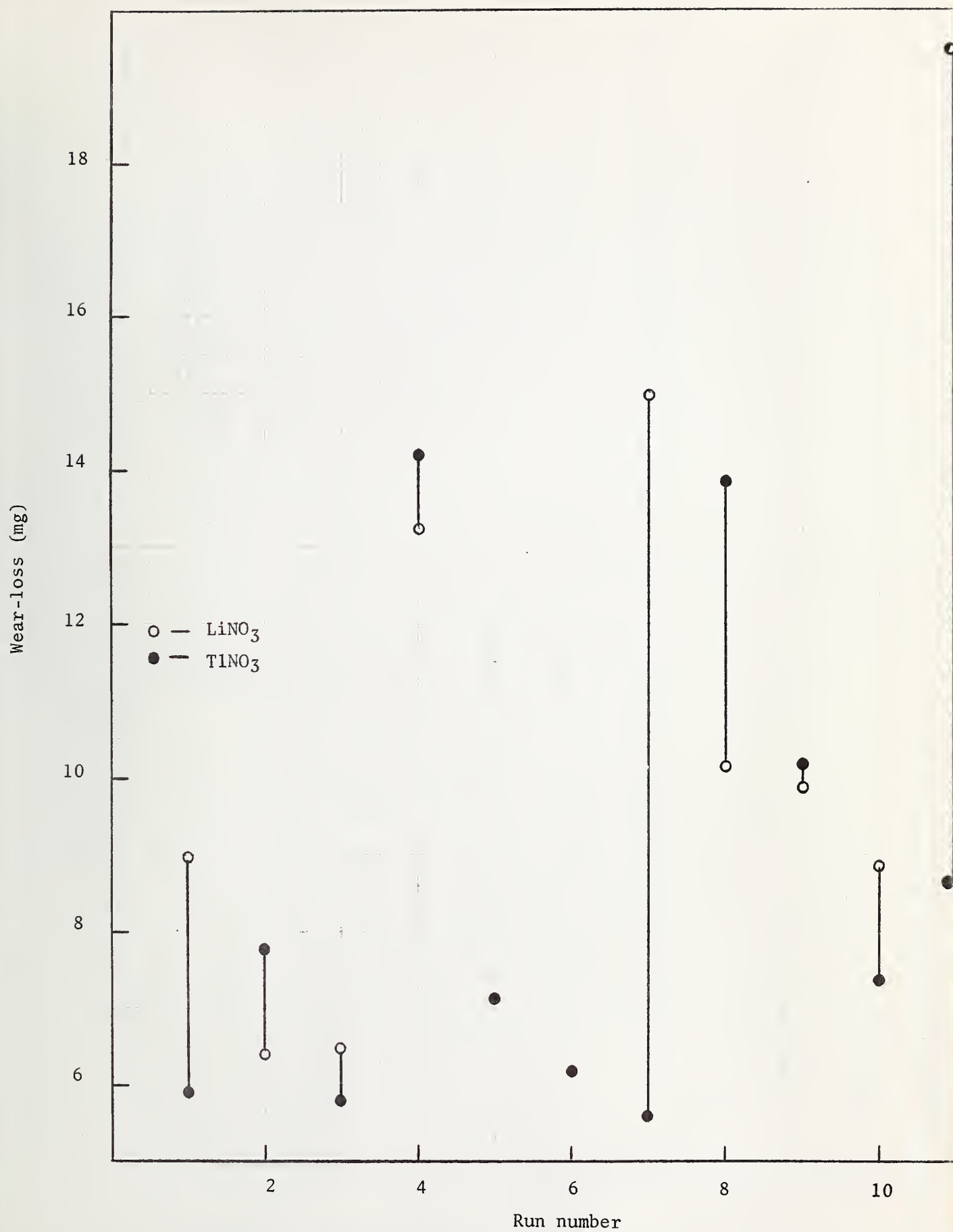


Figure 5. Comparison of effect of bath additives under similar plating conditions.



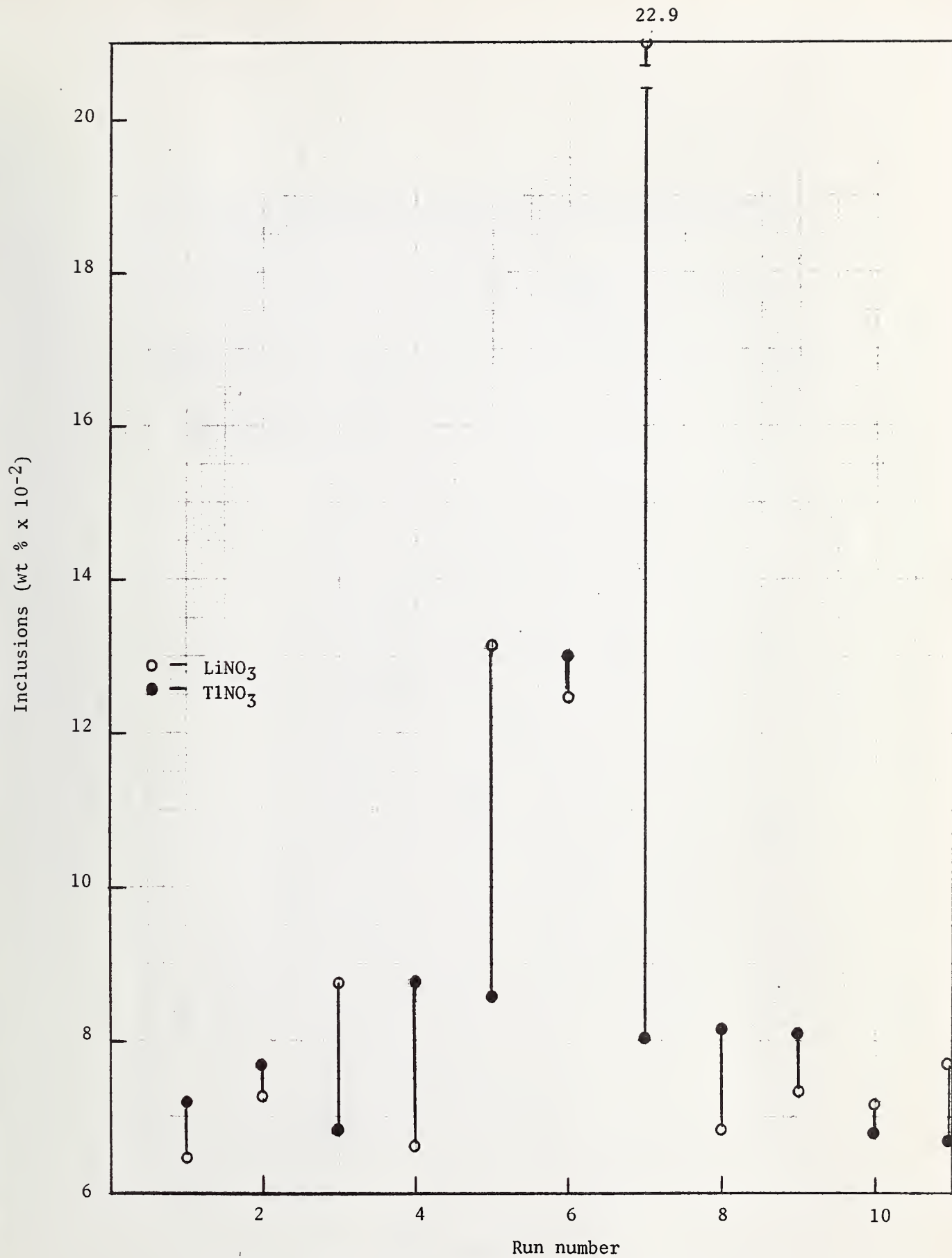


Figure 6. Comparison of effect of additives to Cr bath under similar plating conditions.



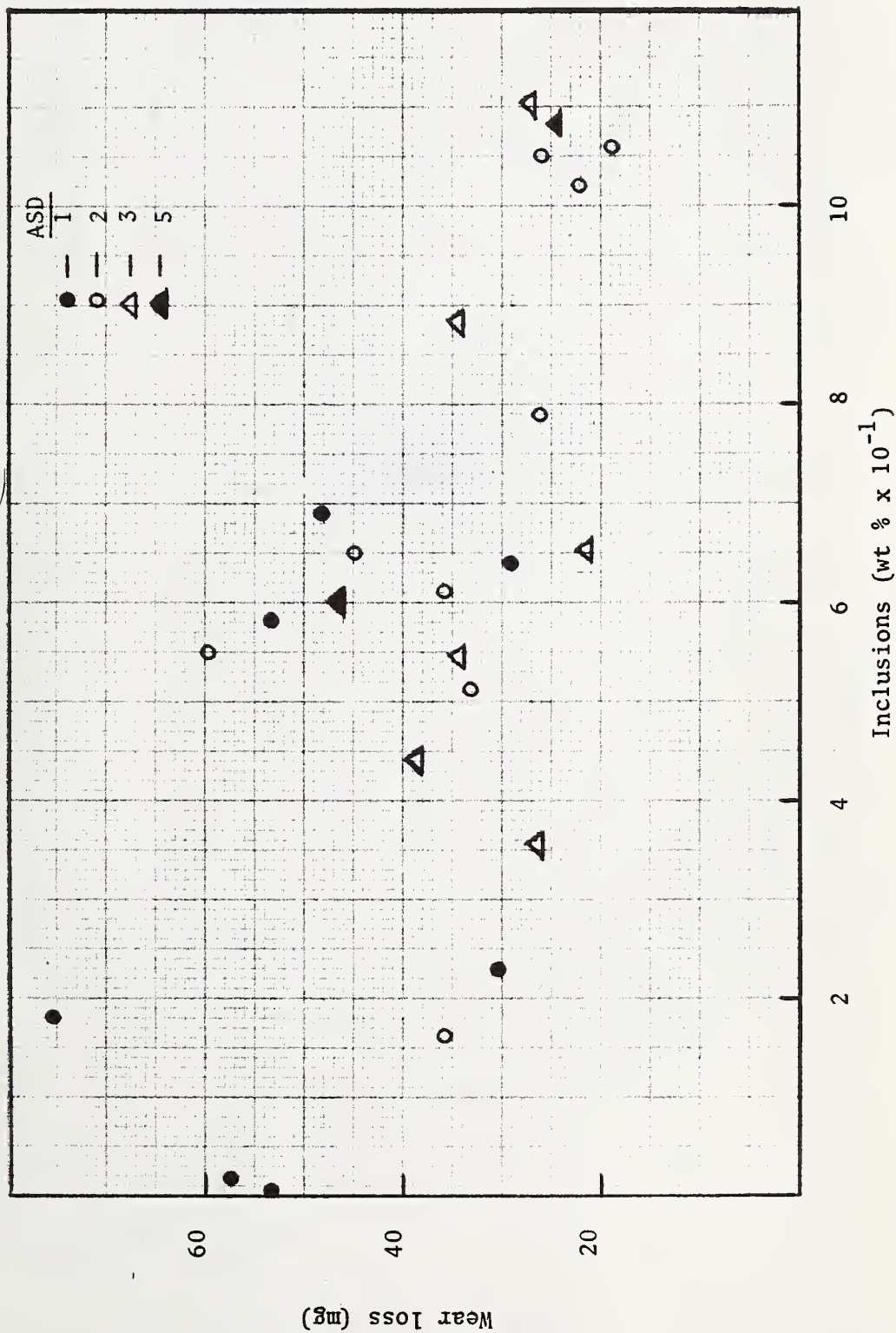
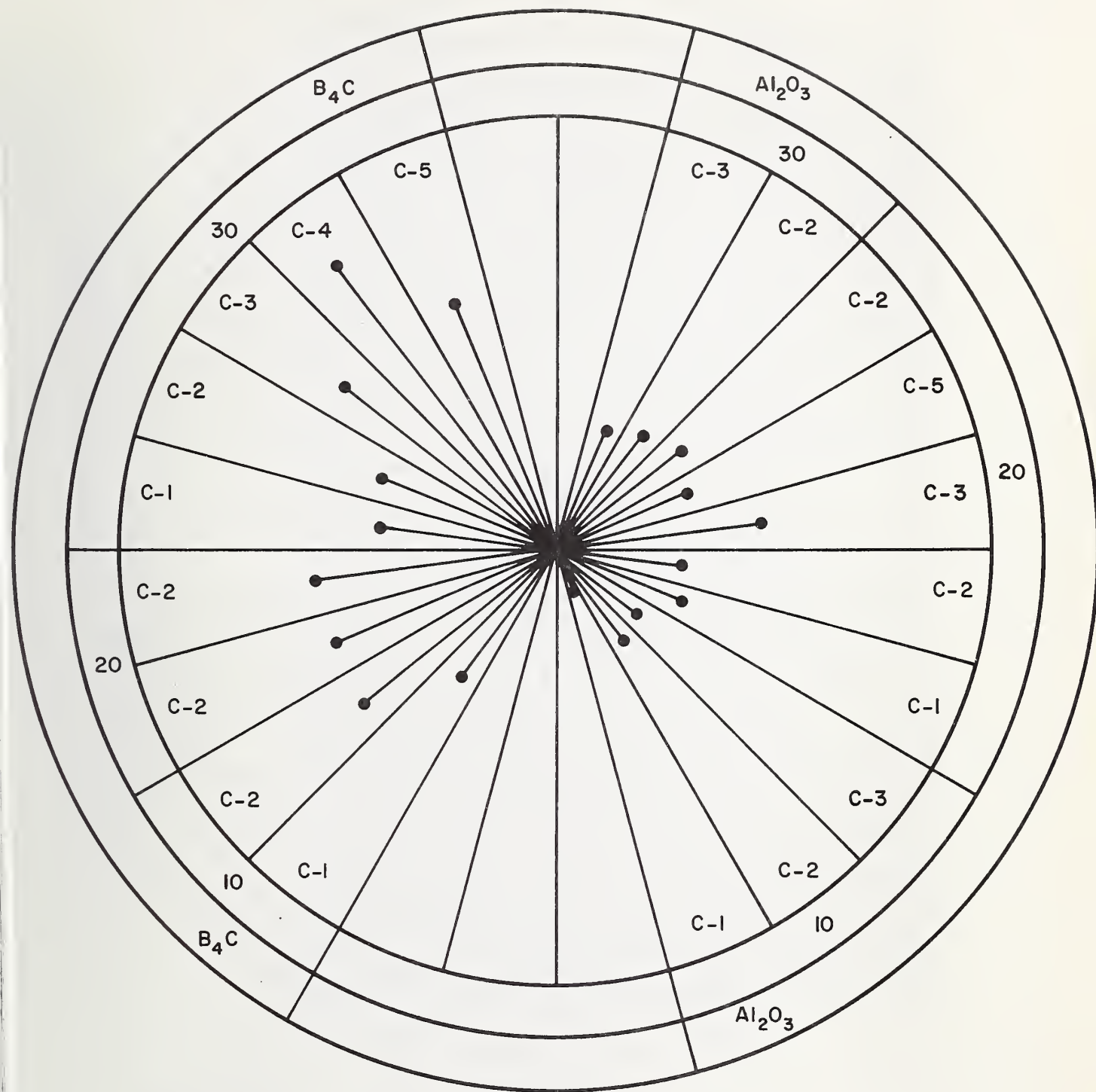


Figure 7. Inclusions versus wear in Cd plated at 24°C in CN bath.





Temp. = 24°C

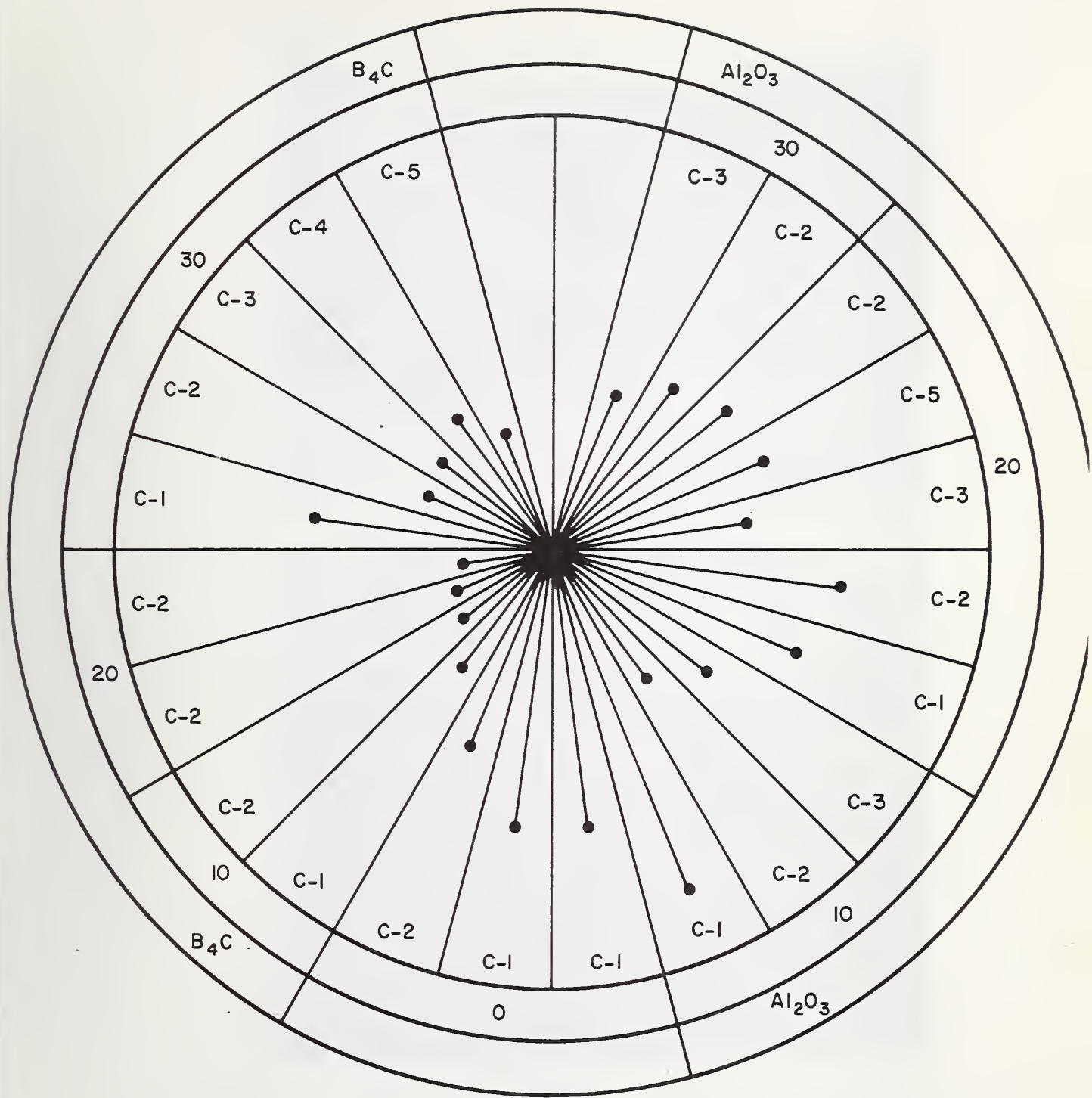
C = Current density in asd

Inside ring = g/l particles in bath

Radii = Inclusions 0.3 wt. %

Figure 8. Amount of inclusions in cadmium deposits.





Temp. = 34°C

C = Current density in asd

Inside ring = g/l particles in bath

Radii = Wear loss  15 mg

Figure 9. Wear-loss of cadmium deposits with included particles.



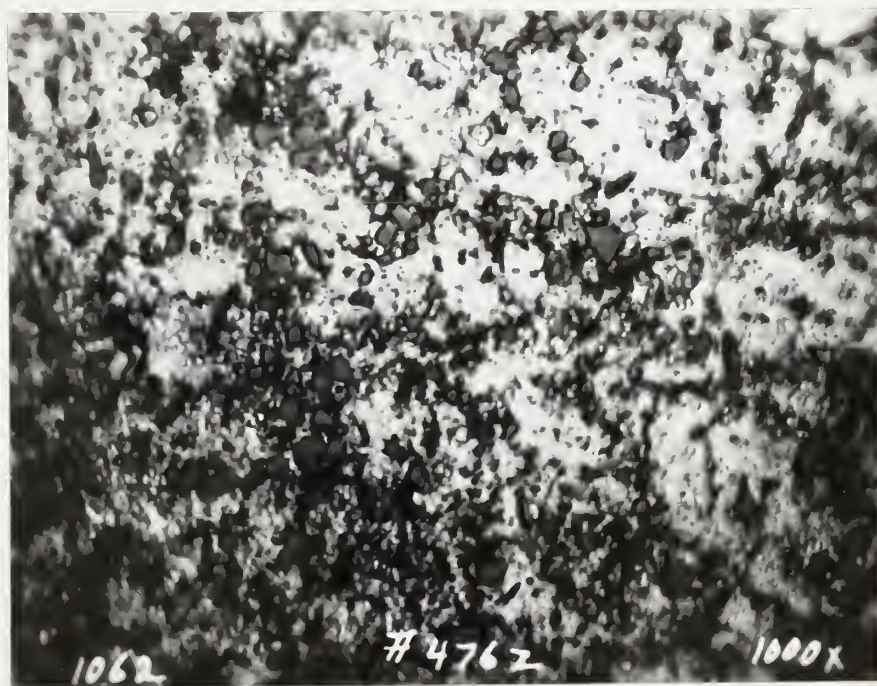


Figure 10. Cadmium (top) and zinc deposits containing B<sub>4</sub>C particles plated from cyanide baths at 24°C/1 and 3 asd respectively. No etch.



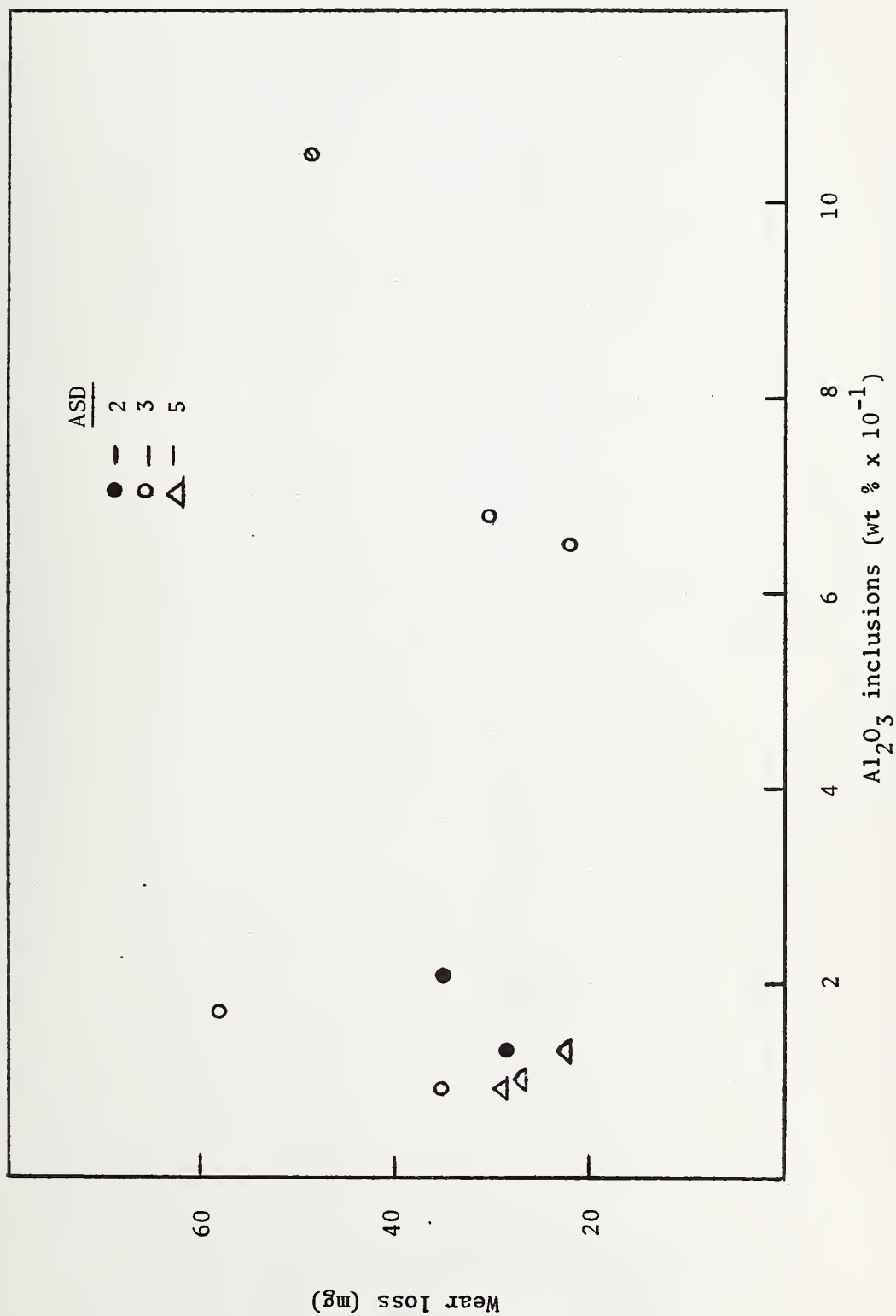


Figure 11. Inclusions versus wear-loss for zinc with included Al<sub>2</sub>O<sub>3</sub> deposited in a cyanide bath at 24°C.



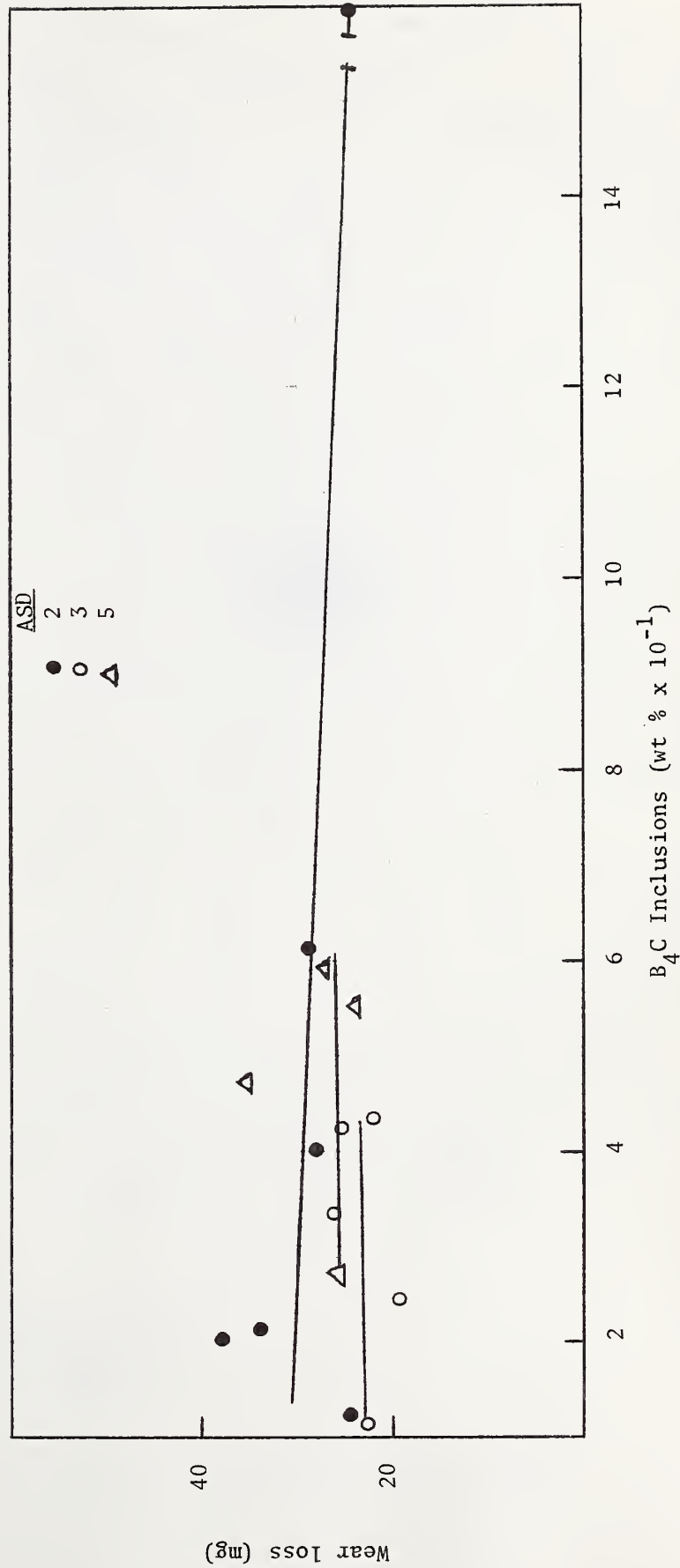
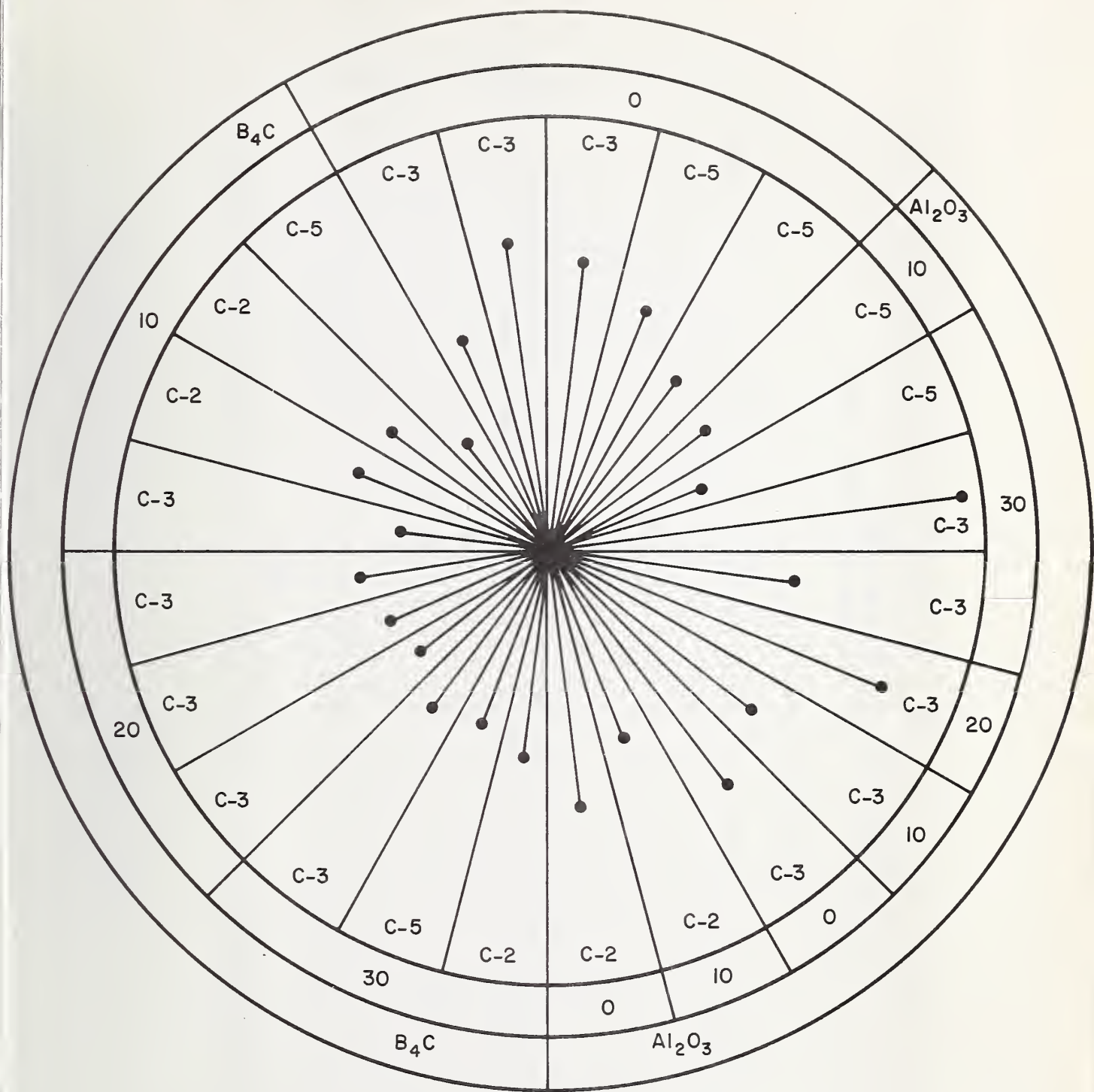


Figure 12. Inclusions versus wear-loss for zinc deposits with included  $B_4C$  from a cyanide bath at  $24^\circ C$ .





Temp. = 24°C

C = Current density in asd

Inside ring = g/l particles in bath

Radii = Wear loss  $\overbrace{\hspace{1cm}}^{10\text{ mg}}$

Figure 13. Wear-loss of zinc deposits with included particles.



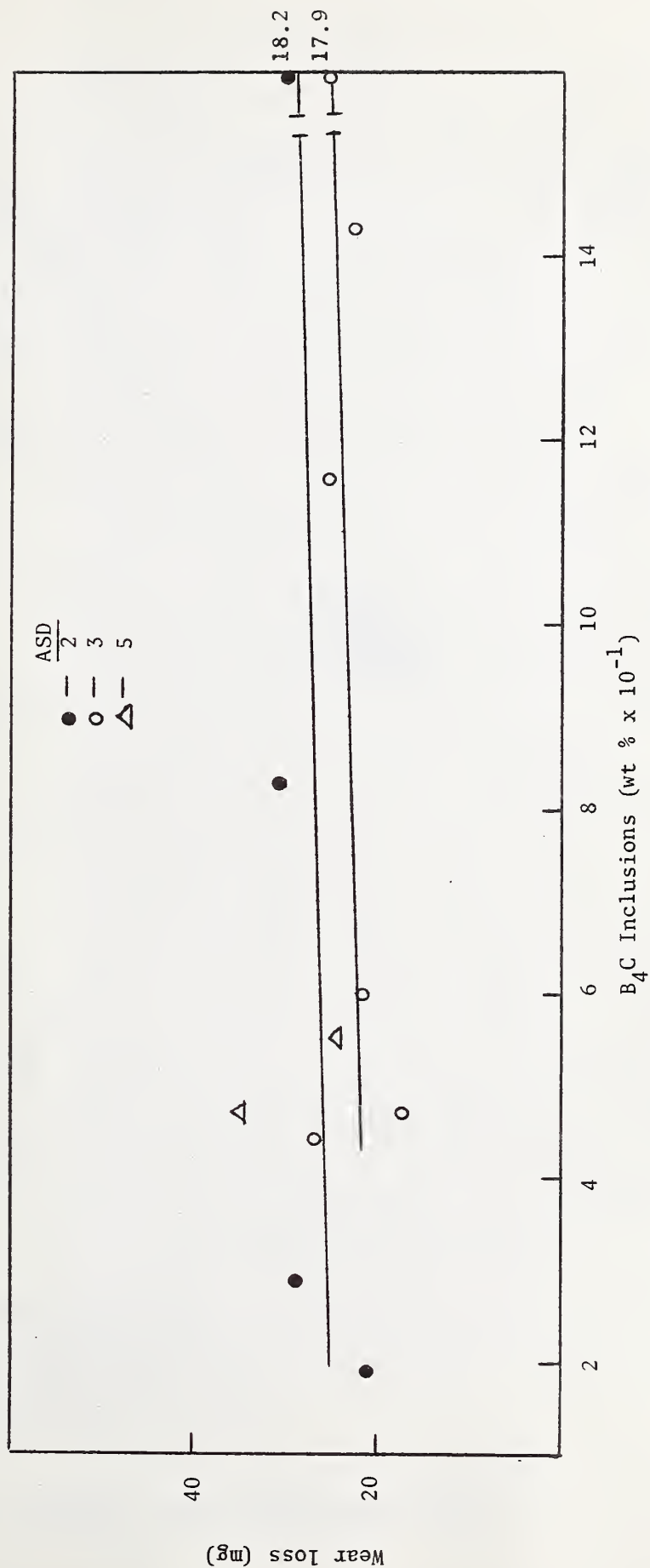
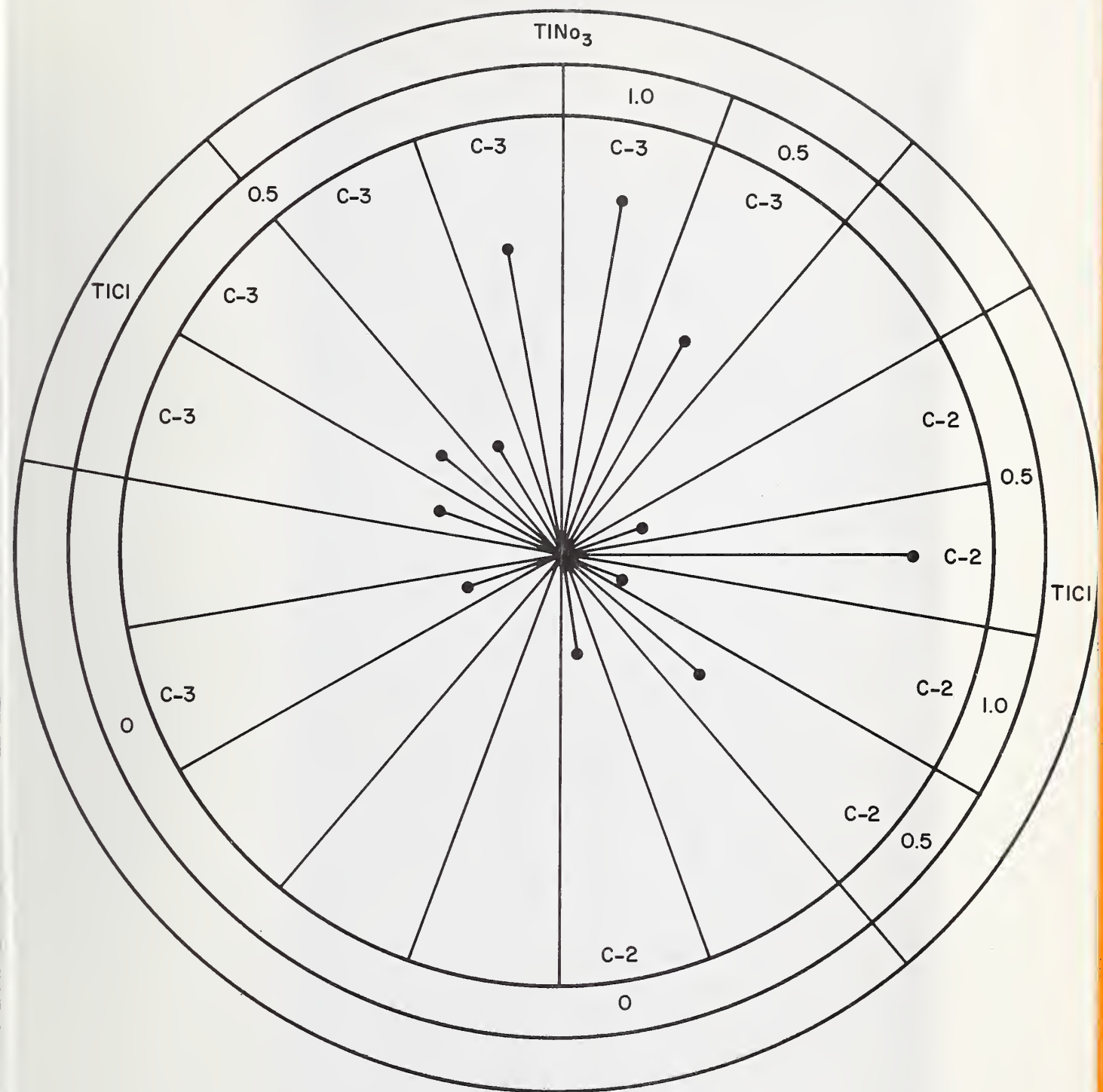


Figure 14. Inclusions in zinc versus wear-loss for deposits plated in a cyanide bath at 24°C using TiNO<sub>3</sub>.





Temp. = 24°C  $B_4C$  - 30 g/l

C = Current density in asd

Inside ring = g/l  $TiNO_3$  or  $TiCl$

Radii = amt. inclusions .40 wt. %

Figure 15. Inclusions in zinc deposits using thallium.





Figure 16. Chromium deposit on inside of stainless steel tube 3/8 inch ID x 20 inches long. Chromium deposited at 45°C/30 asd in tube in vertical position from bath containing 3 g/l Tl NO<sub>3</sub> and 30 g/l B<sub>4</sub>C. Cross-sections taken from top, center, and bottom of tube. Hard particles resist polishing and leave "tails" of raised Cr. No etch.





Figure 17. Heat-treated series. Top 250°C for 2 hrs, center 400°C for 1 hr, bottom 600°C for 1 hr. Chromium deposited on copper from bath containing 3 g/l Tl NO<sub>3</sub>. No etch.



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Several new hard particles were tried with the object of improving wear-resistance of chromium deposits containing included particles over the best previously tried material, tetra-boron carbide. Only hexa-boron ~~chloride~~ <sup>carbide</sup> was slightly better. During a bath-life test 5100 ampere-hours per liter were run through a particle-including chromium bath. Build-up of products of the monovalent-cation additive used was detected but bath performance could be restored to normal by their removal. Heat treatment of deposits showed reduction in wear-resistance of deposits heated to 400°C or over. A caliber 0.30 tube was plated with chromium having included particles with relatively good particle distribution throughout the bore. Deposits of cadmium and zinc with included hard particles showed some improvement in wear-resistance.

## 17. KEY WORDS

Bonding; cement; chromium; composite coatings; deposit hardness; dispersed phase; dispersion hardened; electrodeposition; electro-inclusions; electroplating; monovalent cation; occlusion plating; particle codeposition; particle inclusions; wear resistance.

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